Indian J. Phys. 76A (5), 453-456 (2002)

IJP A
-- an international journal

Study of thermal pressure for alkali halides and geophysical minerals

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Received 17 October 2001, accepted 5 July 2002

Abstract Phenomenological equations of state representing the relationships between pressure and volume have been used to estimate the value of thermal pressure for two alkali halides (NaCl and KCl) and six geophysical minerals (MgO, CaO, Al_2O_3, Mg_2SiO_4, Grossular Garnet, pyrope garnet) along an isobar at zero pressure. Values of thermal pressure at higher temperatures relative to room temperature for the solids under study have been found to present close agreement with the experimental data reported by Anderson.

Keywords Thermal pressure, equation of state, ionic solids, geophysical minerals

PACS Nos. 64.10.+h, 64.30.+t, 65.40.-b

1 Introduction

An equation of state (EOS) for solids can be represented by the following relationship [1]

$$P(V,T) = P(V,T_0) + \Delta P_{th}, \quad (1)$$

where $P(V, T)$ represents the total pressure as a function of volume V and temperature T. $P(V, T_0)$ gives the relationship between pressure and volume at $T = T_0$, the initial temperature usually taken to be the room temperature (300 K). The last term ΔP_{th} in equation (1) is the difference between the values of thermal pressure at two temperatures T and T_0, *i.e.*

$$\Delta P_{th} = P_{th}(T) - P_{th}(T_0). \quad (2)$$

At zero pressure $P(V, T) = 0$, eq. (1) is reduced to

$$\Delta P_{th} = -P(V,T_0). \quad (3)$$

In the present study, we estimate the values of ΔP_{th} for two alkali halides and six geophysical minerals using eq. (3) and taking $P(V, T_0)$ based on two phenomenological EOSs due to Vinet *et al* [2] and Shanker *et al* [3]. The method of analysis is described in Section 2. Results are discussed and compared with experimental data [4] in Section 3.

2. Method of analysis

Vinet *et al* [2] obtained an EOS for solids considering the interatomic potential energy to depend on interatomic distance r as $(1 + ar) \exp(-br)$, where a and b are constants for a given solid. The EOS thus obtained is given as follows

$$P(V,T_0) = 3K_0 x^{-2}(1-x)\exp\left[\frac{3}{2}(K_0'-1)(1-x)\right], \quad (4)$$

where K_0 and K_0' are the isothermal bulk modulus and its pressure derivative, both at $P = 0$, and $x = (V/V_0)^{1/3}$. It has recently been pointed out by Stacey [5] that eq. (4) has already been derived from the Rydberg potential [6] and reported by Stacey *et al* [7] much earlier than Vinet *et al* [2]. Eq. (4) has been found to be close to the concept of universal equation of state. An EOS is truly universal only when it is successful from low to ultra-high pressures for all types of solids irrespective of their chemical bonds [8]. Thus a universal EOS is applicable for different types of solids such as metals, non-metals, rare gas solids and geophysical minerals.

Recently, Shanker *et al* [3, 9] have obtained an EOS using the volume dependence of short range force constant based on interatomic potential energy. The results obtained from the

Shanker EOS have been found to be in close agreement with those based on the Vinet EOS. The Shanker EOS is expressed as follows :

$$P = \frac{K_0(V/V_0)^{4/3}}{} \left| \left| 1 - \frac{1}{t} + \frac{2}{t^2} \right| \{\exp(ty) - 1\} \right.$$

$$+ y \left| 1 + y - \frac{2}{t} \right| \exp(ty) \Big|, \qquad (5)$$

where $t = K_0' - \frac{8}{3}$ and $y = 1 - (V/V_0)$.

Eq. (3) and (4) yield

$$\Delta P_{th} = -3K_0 x^{-2}(1-x) \exp\left[\frac{3}{2}(K_0' - 1)(1-x)\right] \qquad (6)$$

Similarly, eqs. (3) and (5) give

$$\Delta P_{th} = \frac{-K_0(V/V_0)^{-4/3}}{} \left| -\frac{1}{t} + \frac{2}{t^2} \right| \{\exp(ty) - 1\}$$

$$+ y \left| 1 + y - \frac{2}{t} \right| \exp(ty) \Big| \qquad (7)$$

Eqs. (6) and (7) represent the relationship between thermal pressure and change in volume with temperature along an isobar at $P = 0$ [10]. Values of ΔP_{th} can be calculated with the help of eq. (6) or (7) using the values of V/V_0, where V is the volume at temperature T and V_0 is the volume at $T = T_0$, the room temperature (300 K)

3. Results and discussion

Anderson [4] has reported the values of density based on experimental measurements for NaCl, KCl, MgO, CaO, Al_2O_3, Mg_2SiO_4, Grossular Garnet and pyrope Garnet upto quite high temperatures. Values of V/V_0 are obtained from the density data using the relationship $(V/V_0) = (\rho_0/\rho)$ where ρ_0 is the density ρ at $T = T_0$. Values of input data on K_0 and K_0' are given in Table 1. The values of thermal pressure ΔP_{th} calculated from eqs. (6) and (7) are reported in Tables 2-5 alongwith the values of V/V_0. The method of calculating the thermal pressure used in the present study is different from that used by earlier workers as reviewed by Anderson [4]. Values of ΔP_{th} have been estimated using the following relationship [4, 11]

$$\Delta P_{th} = \int_{T_0}^{T} \alpha K_T \, dT \qquad (8)$$

Table 2. Values of thermal pressure ΔP_{th} (GPa) versus temperature T and V/V_0 for NaCl and KCl (a) Calculated from eq. (6), (b) Calculated from eq (7) (c) Based on experimental data [4]

Solid	T (K)	V/V_0	ΔP_{th} (GPa) (a)	(b)	(c)
	300	1	0	0	0
	350	1 0061	0 1436	0.1436	0 14
NaCl	400	1 0127	0 2928	0.2928	0 28
	450	1 0194	0 4379	0 4379	0 43
	500	1 0261	0.5768	0 5769	0 57
	550	1 0335	0 7235	0 7236	0 71
	600	1 0410	0 8651	0 8654	0 85
	650	1 0486	1 0016	1 0022	0 99
	700	1 0568	1 1415	1 1424	1 13
	750	1 0656	1 2835	1 2847	1 27
	300	1	0	0	0
	350	1 0056	0.0935	0 0935	0 09
	400	1 0117	0 1916	0 1916	0 19
	450	1 0175	0 2813	0 2813	0 28
	500	1 0243	0 3822	0 3822	0 37
KCl	550	1 0307	0 4732	0 4733	0 47
	600	1 0377	0 5684	0 5686	0 56
	650	1 0448	0 6606	0 6608	0 65
	700	1 0526	0 7569	0 7574	0 75
	750	1 0605	0 8496	0 8503	0 84
	800	1 0685	0 9385	0 9395	0 93
	850	1 0772	1 0298	1 0313	1 02

Table 1. Values of input data for K_0 (GPa) and K_0' for alkali halides and geophysical minerals taken from reference [4]

	NaCl	KCl	MgO	CaO	Al_2O_3	Mg_2SiO_4	Grossular Garnet	Pyrope Garnet
K_0	24 0	17 0	161 6	110 6	252.0	127 3	166.6	169.4
K_0'	5 38	5 46	4 15	4 85	4.0	4 0	4 0	4 0

Table 3. Values of thermal pressure ΔP_{th} (GPa) versus temperature T and V/V_0 for MgO and CaO (a) Calculated from eq (6), (b) Calculated from eq (7) (c) Based on experimental data [4].

Solid	T (K)	V/V_0	ΔP_{th} (GPa) (a)	(b)	(c)
	300	1	0	0	0
	400	1 0033	0 5288	0.5288	0.54
	500	1 0073	1 1578	1.1578	1 12
	600	1.0112	1 7587	1 7587	1 73
	700	1.0153	2 3775	2 3776	2 35
MgO	800	1 0196	3.0126	3.0127	2 98
	900	1 024	3 6480	3 6482	3 61
	1000	1 0284	4 2691	4 2695	4 24
	1100	1 0331	4 9172	4 9178	4 87
	1200	1 0379	5.5629	5 5638	5 50
	1300	1 0427	6 1927	6 1940	6 12
	1400	1 0476	6 8197	6.8214	6 74
	1500	1 0528	7 4677	7 4701	7 36
	1600	1 0581	8 1104	8 1136	7 97
	1700	1 0635	8 7472	8 7513	8 58
	1800	1 0688	9 3550	9 3601	9 20
	300	1	0	0	0
	400	1 0033	0 3615	0.3615	0 36
	500	1 0066	0 7160	0 7160	0 74
	600	1 0106	1 1367	1 1367	1 13
	700	1 0145	1 5375	1 5375	1 53
	800	1 0186	1 9490	1 9491	1 94
	900	1 0226	2 3410	2 3412	2 34
	1000	1 0267	2 7333	2 7336	2 74
	1100	1 0311	3 1439	3 1444	3.13
	1200	1.0356	3 5529	3 5536	3.53

Table 4. Values of thermal pressure ΔP_{th} (GPa) versus temperature T and V/V_0 for Al_2O_3 and Mg_2SiO_4. (a) Calculated from eq (6), (b) Calculated from eq (7) (c) Based on experimental data [4]

Solid	T (K)	V/V_0	ΔP_{th} (GPa) (a)	(b)	(c)
	300	1	0	0	0
	400	1 0018	0.4516	0 4516	0 45
	500	1 004	0 9980	0 9980	0 98
	600	1 0063	1 5629	1 5629	1 55
	700	1 0083	2 0488	2 0488	2 15
Al_2O_3	800	1 0114	2 7924	2 7925	2 76
	900	1 014	3 4073	3 4074	3 43
	1000	1 0168	4 0606	4 0607	4 01
	1100	1 0195	4 6819	4 6821	4 64
	1200	1 0223	5 3174	5 3177	5 23
	1300	1 0252	5 9663	5 9667	5 93
	1400	1 0279	6 5620	6.5625	6 59
	1500	1 0308	7 1928	7 1935	7 24
	1600	1 0337	7 8146	7.8155	7 91
	1700	1 0364	8 3854	8 3866	8.57
	1800	1 0394	9 0106	9 0121	9 24
	300	1	0	0	0
	400	1 0028	0.3540	0 3540	0 36
	500	1 0059	0.7401	0 7401	0 75
	600	1 0094	1 1689	1 1689	1 16
Mg_2SiO_4	700	1 0129	1 5903	1 5903	1 57
	800	1 0164	2 0044	2 0044	1 98
	900	1 0199	2 4112	2 4113	2 40
	1000	1 0238	2 8563	2 8564	2.83
	1100	1 0277	3 2927	3.2929	3 25
	1200	1 032	3 7641	3.7645	3 69
	1300	1 0363	4 2254	4 2259	4 13
	1400	1 0407	4 6872	4 6880	4 50
	1500	1 0451	5 1389	5 1400	5 07
	1600	1 0498	5 6104	5 6119	5 43
	1700	1 0547	6 0903	6 0923	5 87

Values of ΔP_{th} have thus been obtained with the help of eq (8) using experimental values of thermal expansivity α and isothermal bulk modulus K_T. The results based on eq. (8) have also been included in the Tables for the sake of comparison. It is found that there is good agreement between the calculated and experimental values of ΔP_{th} for the solids under study.

It is worth mentioning here that the results obtained in the present study are useful for investigating further the thermoelastic behaviour of ionic solids and geophysical minerals. The values of thermal pressure calculated here may be used to study the thermal expansivity and isothermal bulk modulus for the solids under the effect of high pressure and high temperature.

Table 5. Values of thermal pressure ΔP_{th} (GPa) versus temperature T and V/V_0 for Grossular Garnet and Pyrope Garnet (a) Calculated from eq (6) (b) Calculated from eq (7) (c) Based on experimental data [4]

Solid	T (K)	V/V_0	ΔP_{th} (GPa) (a)	(b)	(c)
	300	1	0	0	0
	400	1 0022	0 3646	0 3646	0 36
	500	1 0044	0 7253	0 7253	0 75
	600	1 0073	1 1947	1 1947	1 16
Grossular	700	1 0098	1 5939	1 5939	1 57
Garnet	800	1 0126	2 0351	2 0351	1 98
	900	1 0155	2 4856	2 4857	2 40
	1000	1 0184	2 9296	2 9297	2 83
	1100	1 0213	3 3672	3 3674	3 25
	1200	1 0242	3 7985	3 7987	3 69
	1300	1 0274	4 2672	4 2675	5 40
	300	1	0	0	0
	400	1 0027	0 4543	0 4543	0 42
	500	1 0054	0 9025	0 9025	0 87
Pyrope	600	1 0082	1 3610	1 3610	1 34
Garnet	700	1 0112	1 8451	1 8451	1 81
	800	1 0142	2 3220	2 3221	2 28
	900	1 0173	2 8074	2 8075	2 75
	1000	1 0203	3 2699	3 2701	3 23
	1100	1 0238	3 8009	3 8011	3 71
	1200	1 0269	4 2634	4 2637	4 19

Acknowledgments

The Referee's comments have been found useful in revising the manuscript. Author is thankful to Prof. Jai Shanker, Institute of Basic Sciences, Agra, for his valuable comments.

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